Final Report for AOARD Grant FA2386-08-1-4119

"**Focused Ion Beam Milling Applied in Future Tunable-Wavelength Nano-LED's Fabrication**"

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Abstract:

We have applied Focused ion beam milling followed by KOH wet etching method in fabricating future tunable-wavelength nano-light emitting diode (LED) comprised of nanopillars. We could successfully achieve not only site-controlled but size-controlled LED arrays. Light extraction was enhanced greatly for the LEDs with the nano-pillar arrays. The high crystallinity of the nano-pillars fabricated by our method ensures the high LED efficiency. In addition, we showed only slight degradation on the electrical behavior of a single nano-pillar LED compared to the pristine LED. Finally, we demonstrated EL enhancement of ~3.1% for the LED with only 1% patterned area.

Introduction:

Focused ion beam (FIB) is an emerging technology with that complicated three-dimensional architecture can be designed at nanoscale smaller than 50 nm. The milling process has also been employed to fabricate patterns on III-V semiconductors for prototyping waveguides, distributed Bragg reflectors (DBR), photonic crystals and single-photon devices.[1-5]

We have developed a technique of self-masking lithography for making high aspect-ratio nanopillars by using a volume swelling phenomenon during beam-material interactions. When this method was applied in light emitting diodes (LED) devices, a single pillar or arrays of pillars comprising InGaN/GaN multiple quantum wells (MQW) as nano-LEDs with high light extraction were successfully made.

Experiment:

The detailed experimental procedure is described as follows:

1) Preparation of MQW samples: InGaN/GaN MQW samples with various compositions grown by metal-organic chemical vapor deposition can be acquired from my collaborators in NCKU and in Genesis Photonics Incorporation.
2) Focused ion beam prestructuring: InGaN/GaN MQWs embedded GaN pillar/pyramid arrays were fabricated by FIB pre-structuring. Ga ions of 10-30 keV were employed to partially remove the nitride materials according to the preset drawing in bitmap format, and controlling the beam dwell time and the ion dosage will result in pillar/pyramid structures with various aspect-ratios.
3) Side surface trimming of the FIB-milled pillars: ion irradiated surface damages of the pillars were subsequently removed by KOH etching. In addition to the removal of the amorphous layer, of which the thickness depends on the FIB milling recipe, the pillar/pyramid size could be further reduced resulting from anisotropic etching. The normal of the preferred etching plane was found to be perpendicular/inclined to the pillar/pyramid axis, which in turn made the pillar size controllable by varying the KOH treatment time.
4) Structure and optical characterizations of after-etched pillars: FIB-milled pillars followed by KOH etching are investigated by transmission electron microscopy (TEM) for structure analysis and cathodluminescence (CL) for optical characterization.
5) The MQW nanopillar/nanopyramid arrays were then buried in spin-on glass (SOG) for the isolation of individual nanopillars/nanopyramids, and for the purpose of bringing the p-type

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14. ABSTRACT
This is a report on the development of a technique of self-masking lithography for making high aspect-ratio nanopillars by using a volume swelling phenomenon during beam-material interactions.

15. SUBJECT TERMS
Light Emitting Devices, Focused Ion Beam Milling, Multiple Quantum Wells

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pillars/pyramids into contacts with the p-type electrodes. Fig. 1 shows a cross-sectional schematic diagram of the fabricated InGaN/GaN MQW nanopillar/nanopyramid LED structure. The fabrication processes are almost identical to those of conventional broad area LEDs, except for the SOG coating process.

6) Electrical and opto-electrical properties: The MQW nanopillar/nanopyramid arrays were fabricated into LED structure. The electrical and opto-electrical properties of both single and multipillar arrays are studied in detail in order to realize the light enhancement mechanisms.

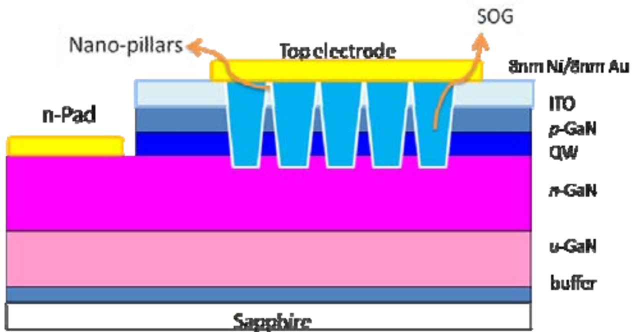


Fig.1 Cross-sectional schematic of the nano-LED structure

Results and Discussion:

The results are divided into three parts: Focused Ion Beam Milling Applied in LED wafer, Emission properties of nanorods by FIB milling and Nanorod-based LEDs

Focused Ion Beam Milling Applied in LED wafer:

We have applied the Focused Ion Beam milling technique directly on InGaN/GaN MQW LED wafers. By setting up different bitmaps for patterning, various patterned 1D nano-pillar arrays were fabricated directly on the InGaN/GaN MQW LED wafer by Gallium (Ga^+) beam milling. Figure 2 shows various bitmaps that were designed for different pattering. Here, the dot-array pattern may produce large-area 0D dot-array or 1D rod-array structure depending on ion beam milling in different depth, which may contribute to light extraction enhancement of the InGaN/GaN MQW LED surface.

Figure 3 shows a scanning electron microscopy (SEM) image of as-milled nano-pillars on an InGaN/GaN MQW LED wafer with the dot-array pattern. Apparently, upon ion beam milling, huge damaged surface layers with bumps on the tops of the nano-pillars were formed due to ion-beam/crystalline structure interaction. Almost one nanorod bears one bump on top after FIB modification. Electron energy loss spectroscopy in TEM as shown in Figure 4 reveals that the bump is comprised of oxygen-rich amorphous layer, while nitrogen still is retained in the nano-pillar itself. During high energy ion beam bombardment, Ga-N bonding is possibly disintegrated and nitrogen is evaporated while oxygen from the chamber residual gas might react with Ga to form amorphous gallium oxide.

The surface amorphous layer on LED would exert serious adverse effect on light emission properties, and we developed a simple KOH wet chemical etching method to successfully remove the damage layer and the bump. By carefully controlling the etching time and solution temperature, we could not only etch the damage layer thoroughly but the nano-pillars were thinned continuously as shown in Figure 5. Not only site-controlled, but also size-controlled has been achieved! TEM images in Figure 6 confirm the high perfection of crystallinity in the nano-pillars all the way to the edges after FIB milling with KOH wet etching. Furthermore, another important issue that might be induced by FIB milling is internal stress, especially in GaN-based LEDs. We analyze this issue by showing TEM images in Figure 7 imaged with the (200) two-beam condition, from which little strain contrast and no defects can be observed in the nano-pillar, indicating that these processes wouldn’t induce extra stress to the nano-pillars. These results ensure us that applying FIB milling followed by KOH wet etching is promising in fabricating future tunable-wavelength nano-LEDs fabrication.

Light emission properties of nanopillars by FIB milling:

As we applied the FIB milling technique in the future tunable-wavelength nano-LED, we must realize how well the nanopillars can enhance the optical property. Figure 8 (a) shows the CL spectra of a pristine wafer compared with nano-pillars before and after the surface damaged layers being

removed by wet etching. It is clearly evident that the damaged layer hinders the emission from MQWs significantly and light emission can be enhanced by three times after the removal of this layer. Figure 8 (b) and (c) are showing the corresponding SEM images, respectively. Figure 8 (d) shows the SEM and CL images extracted from wavelength of 420nm. It is clearly evident that the MQW emission and the nanorod positions are in good coincidence, proving the MQW emission is truly originated from each individual nanopillars.

Nanorod-based LEDs:

Nanorods array structure fabricated by FIB milling followed by KOH wet etching has been successfully developed for InGaN/GaN LED devices, where the diameters of nanorods could be tuned easily by wet etching time as we mentioned before. Here we applied this technique directly on the LED surface, then we investigated the electrical and opto-electrical properties of individual nanorod in detail. We employed conductive AFM to study IV of individual nano-pillars and the experimental setup is shown in Figure 9. Figure 10 (b) shows the results of IV characteristics of 5 different nanorods as marked in Figure 10 (a). The results show that they all exhibit almost the same IV behaviors, revealing the high stability of the process. The turn-on voltage of the nanorods extracted from the IV curves is around 4 volts, which is slightly higher than ~3.63V for the original LED as shown in Figure 10 (c). The higher turn-on voltage may be attributed to lower shunt resistance of the nanorods. Another important LED quality index is the slope after the LED is “on”, which is representative of the total series resistance. Figure 10 (b) shows only slight deviations for the slopes among all the curves, suggesting that the total resistance of individial nanorods is similar. With the IV characteristics, it is confirmed that these nanorod fabrication processes only affect the electrical performance of LED very slightly.

We have further made a nano-LED device comprised of nano-pillar arrays with electrodes based on the schematic diagram shown in Figure 1. Figure 11 shows the EL spectrum of a typical nano-LED device and demonstrates light extraction enhancement of ~3.1% at peak wavelength λ_p=448nm, although the patterned area only occupies 1% of total luminescence area due to the processing time limit. There are a few possible reasons responsible for only slight enhancement in EL intensity, compared to much higher enhancement in CL intensity. One is the lack of a transparent conductive film. The Ni/Au alloy film used here could only serve as the Ohmic-contact material but not good for transparent. Another one is the small patterned area (~1%) that is effective in the light enhancement. With further improvement, even higher enhancement on light extraction can be expected.

What’s in the future?

As we could manipulate the nanorod diameter with ease, nanorods of a few nanometers in diameter could be expected. Up to now, we have fabricated the smallest nanorods with the diameter around 30nm, which has not exhibited quantum confinement size effect in our experiments yet. When approaching smaller, the emission light wavelength can be tuned simply with processing time rather than going through tedious growth procedures for different chemistry. In addition, we need to develop a large area patterning technique with the concept of FIB milling, so that the light extraction enhancement from a nano-LED can be maximized.

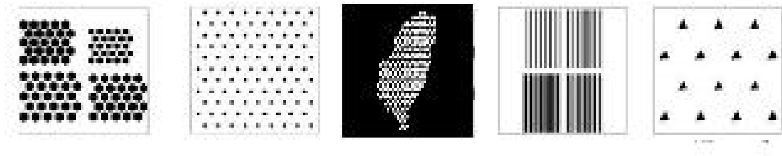


Figure 2: Various bitmaps for 1D nano-pillar pattering in FIB.

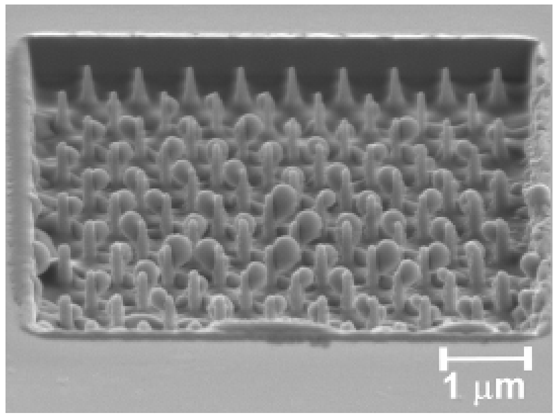


Figure 3: SEM image of the as-milled InGaN/GaN MQW LED wafer

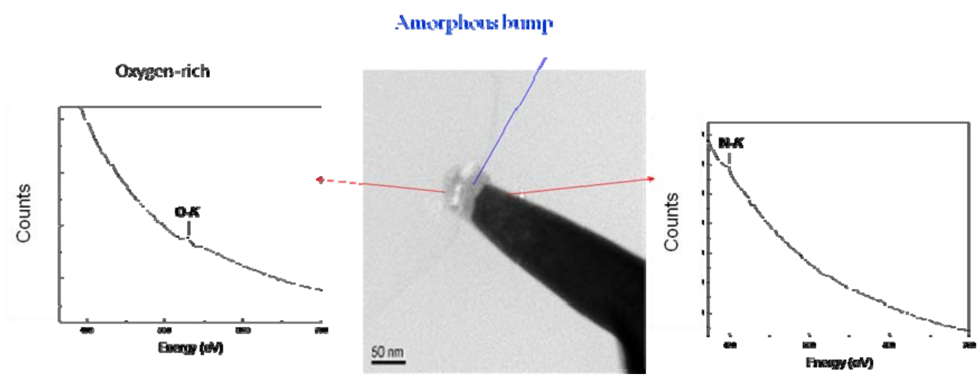


Figure 4: TEM image of one nano-pillar (middle) with EELS spectra from the amorphous bump (left) and the nanorod body (right) as arrowed

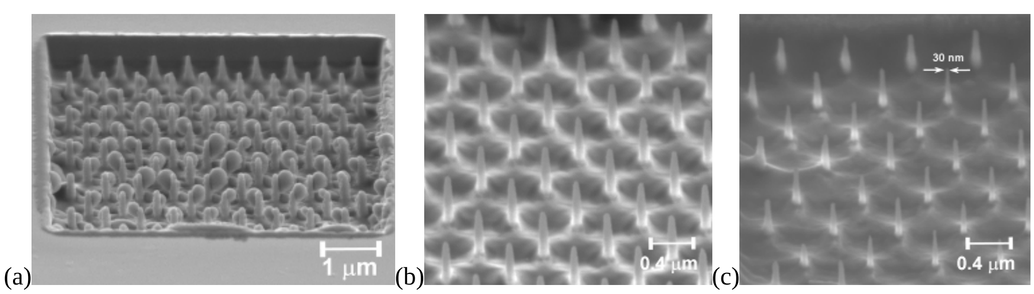


Figure 5: (a) as-milled nanopillar array (b) nanopillars after brief KOH etching (c) nanopillars of smaller size (~30nm) after further KOH etching

(a) (b)

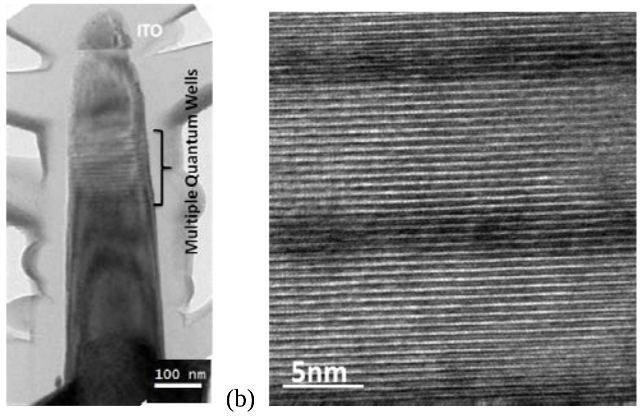


Figure 6: (a) TEM bright field image of a nanopillar (b) High-resolution image of multiple quantum wells in the nanopillar

(a) (b)

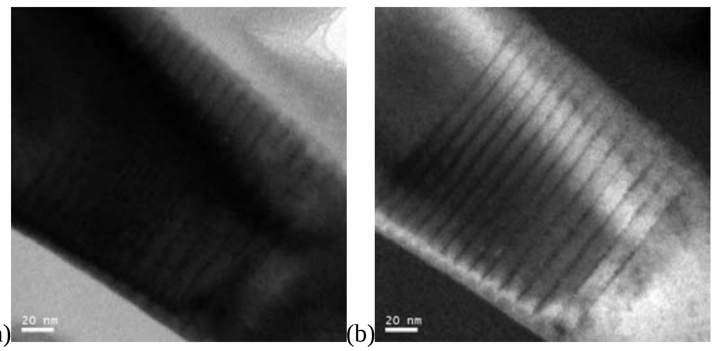


Figure 7: (a) TEM bright field image (b) dark field image of a single nano-pillar containing MQWs after FIB milling with chemical etching at (002) two beam condition

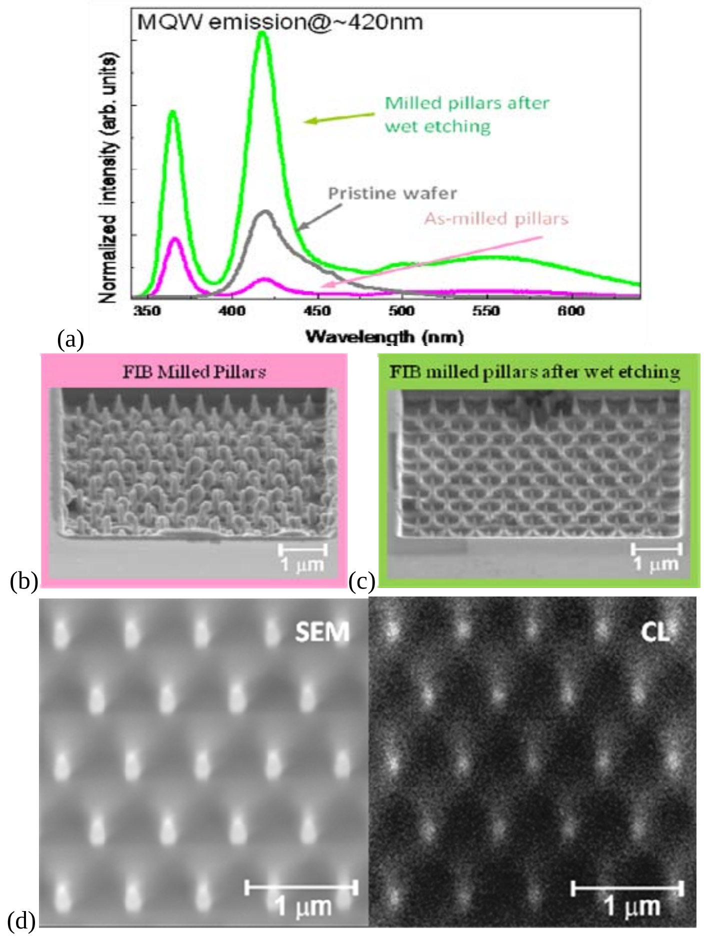


Figure 8: (a) CL spectra of a pristine wafer and nanopillars before and after the surface damaged layers being removed by wet etching; (b) & (c) SEM tilted images of the corresponding as-milled and wet-etched nanopillars; (d) SEM and CL image at λ ~420nm

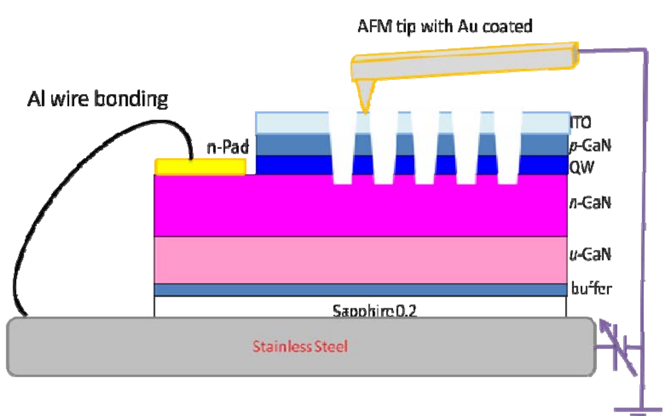
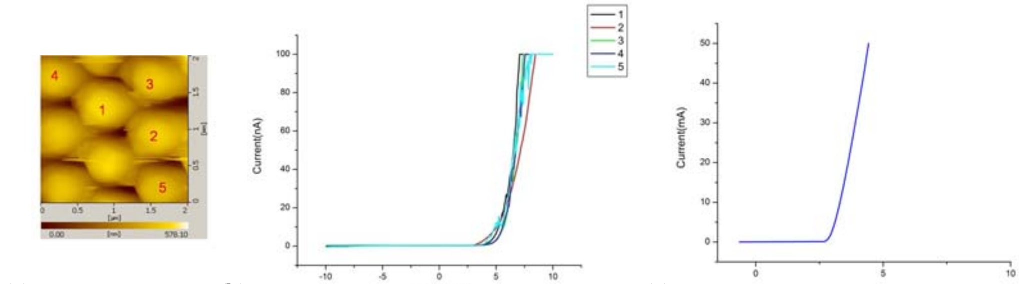


Figure 9: Equipment setup for conductive AFM measurement.



(a) (b) (c)

Figure 10: (a) AFM image of nano-pillar arrays; (b) IV curves of 5 different nano-pillars in (a) compared with (c) original LED IV curve

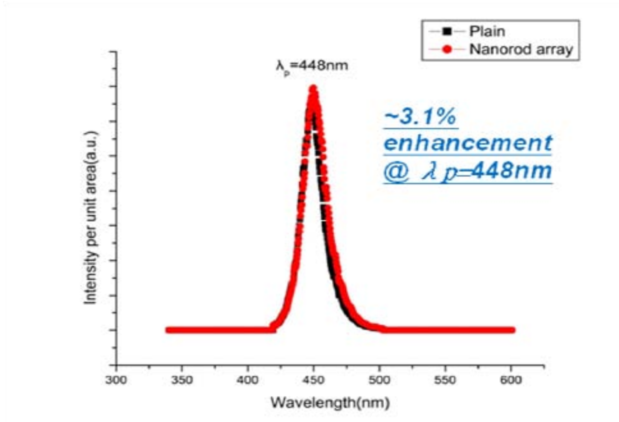


Figure 11: EL spectrum of the original LED (plain) and nano-LED (nanorod arrays). Note that the nanorod array area occupies only 1% of total luminescence area.

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List of Publications:

1. Shang-En Wu, S. Dhara, Tao-Hung Hsueh, Yi-Feng Lai, Cheng-Yu Wang, Chuan-Pu Liu, Journal of Raman Spectroscopy, 40, 2044-2049 (2009)
2. Shang-En Wu, Yu-Wen Huang, Tao-Hung Hsueh, and Chuan-Pu Liu, Japanese Journal of Applied Physics, 47, 4906-4908 (2008)
3. Shang-En Wu, Tao-Hung Hsueh, Chuan-Pu Liu, Jinn-Kong Sheu, Wei-Chih Lai, and Shoou-Jinn Chang, Japanese Journal of Applied Physics, 47, 3130-3133 (2008)

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